



EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY SOLDIER AND BIOLOGICAL CHEMICAL COMMAND

ECBC-TR-281

**DOMESTIC PREPAREDNESS PROGRAM:
EVALUATION OF THE AGILENT
GAS CHROMATOGRAPH - FLAME PHOTOMETRIC DETECTOR/
MASS SELECTIVE DETECTOR (GC-FPD/MSD) SYSTEM
AGAINST CHEMICAL WARFARE AGENTS
SUMMARY REPORT**

**Terri L. Longworth
John M. Baranowski
Kwok Y. Ong**

RESEARCH AND TECHNOLOGY DIRECTORATE

May 2003

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20030910 110



Aberdeen Proving Ground, MD 21010-5424

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 2003 May	3. REPORT TYPE AND DATES COVERED Final; 01 Jan – 01 Oct
4. TITLE AND SUBTITLE Domestic Preparedness Program: Evaluation of The Agilent Gas Chromatograph - Flame Photometric Detector/Mass Selective Detector (GC- FPD/MSD) System Against Chemical Warfare Agents, Summary Report		5. FUNDING NUMBERS NONE
6. AUTHOR (S) Longworth, Terri L.; Baranoski, John M.; and Ong, Kwok Y.		
7. PERFORMING ORGANIZATION NAME (S) AND ADDRESS (ES) DIR, ECBC, ATTN: AMSSB-RRT-AT, APG, MD 21010-5424		8. PERFORMING ORGANIZATION REPORT NUMBER ECBC-TR-281
9. SPONSORING/MONITORING AGENCY NAME (S) AND ADDRESS (ES) DIR, ECBC, ATTN: AMSSB-REN-HD, APG, MD 21010-5424		10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES		
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) This report characterizes the chemical warfare agent (CWA) detection potential of the commercially available Agilent gas chromatograph-flame photometric detector/mass selective detector (GC-FPD/MSD) linked to a Dynatherm system. This system is a thermal desorption, sample concentrating GC-FPD/MSD. The system was tested against HD, GB, and GA with the intent to detect the AEL level concentration. This report provides the emergency responders concerned with CWA detection and verification an overview of the capabilities of the system. The system is planned for use in a mobile analytical laboratory.		
14. SUBJECT TERMS HD Gas Chromatograph GB Mass Spectrometry GA Detector testing GC-FPD/MSD		15. NUMBER OF PAGES 25
		16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
		20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

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PREFACE

The work described in the report was authorized under the Expert Assistance (Equipment Test) Program for the U.S. Army Soldier and Biological Chemical Command (SBCCOM) Program Director for Domestic Preparedness. This work was started in January 2001 and completed in October 2001.

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Acknowledgments

The authors acknowledge Juan C. Cajigas, Rafael M. Martinez, Jacob Barnhouse, and Elaina H. Harrison, U.S. Army Edgewood Chemical Biological Center (ECBC) for their assistance in performing agent testing and data collection; and Frank DiPietro (ECBC) for his assistance in test planning, acquisition, and review.

The authors also thank Agilent (Columbia, MD) for making the system available to support the evaluation. Special thanks are extended to Wayne Abrams, Hernan Diaz, and Bill Arnold for their expert advice and assistance during the evaluation.

The authors are grateful to the following members of the Expert Review Panel for Equipment Testing for their constructive reviews and comments:

Dr. Jimmy Perkins, University of Texas School of Public Health, San Antonio, TX

Dr. Bruce A. Tomkins, Organic Chemistry Section, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

Leo F. Saubier, Battelle Memorial Institute, Edgewood Operations, Aberdeen, MD

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SUMMARY REPORT**

1. INTRODUCTION

The Department of Defense (DOD) formed the Domestic Preparedness (DP) Program in 1996 in response to Public Law 104-201. One of the objectives is to enhance federal, state, and local capabilities to respond to nuclear, biological, and chemical (NBC) terrorism incidents. Emergency responders who encounter either a contaminated or a potentially contaminated area must survey the area for the presence of either toxic or explosive vapors. Presently, the vapor detectors commonly used are not designed to detect and identify chemical warfare (CW) agents. Little data are available concerning the capability of these commonly used, commercially available detection devices to detect CW agents. Under the DP Expert Assistance (Test Equipment) Program, the U.S. Army Soldier and Biological Chemical Command (SBCCOM) established a program to address this need. The Applied Chemistry Team (ACT), Research and Development Directorate, U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, performed the testing. ACT is tasked with providing the necessary information to aid authorities in selecting detection equipment applicable to their needs.

Reports of the instrument evaluations are posted on the Homeland Defense website (<http://hld.sbccom.army.mil/>) for public access. Instruments evaluated and reported since 1998 include the following:

- MiniRAE plus from RAE Systems, Incorporated (Sunnyvale, CA)
- Passport II Organic Vapor Monitor from Mine Safety Appliance Company (Pittsburgh, PA)
- PI-101 Trace Gas Analyzer from HNU Systems, Incorporated (Newton, MA)
- TVA 1000B Toxic Vapor Analyzer (PID and FID) from Foxboro Company (Foxboro, MA)
- Draeger Colorimetric Tubes (Thioether and Phosphoric Acid Ester) from Draeger Safety, Incorporated (Pittsburgh, PA)
- Photovac MicroFID detector from Perkin Elmer Corporation (Wellesley, MA)
- MIRAN SapphiRe Air Analyzer from Foxboro Company (Foxboro, MA)
- MSA Colorimetric Tubes (HD and Phosphoric Acid Ester) from Mine Safety Appliances Company (Pittsburgh, PA)
- M90-D1-C Chemical Warfare Detector from Environics OY, Finland
- APD2000 Detectors from Environmental Technologies Group, Incorporated (Baltimore, MD)
- SAW MiniCAD mkII from Microsensor Systems, Incorporated (Apopka, FL)

- UC AP2C Monitor from Proengin, Incorporated, France
- ppbRAE Photo-Ionization Detector from RAE Systems, Incorporated (Sunnyvale, CA)
- SABRE2000 detector from Barringer Technologies, Incorporated (Warren, NJ)
- CAM (Type L) from Graseby Dynamics Ltd., United Kingdom

In 2001, the evaluation of instruments continued using test items that were loaned to the DP program by their respective manufacturers. Viable candidate instruments were required to pass a pre-screening test. In exchange, the instruments were evaluated under the DP protocol, and the manufacturers were permitted to take data during the evaluations. Instruments evaluated include the following:

- VaporTracer System from Ion Track Instruments, Incorporated (Wilmington, MA)
- HAZMATCAD from Microsensor Systems (Apopka, FL)
- GC-FPD/MSD with Dynatherm System from Agilent (Columbia, MD)
- Scentoscreen GC from Sentex Systems, Incorporated (Ridgefield, NJ)

Each of these evaluations will be reported separately. This report pertains to the evaluation of the Agilent GC-FPD/MSD with Dynatherm system.

2. OBJECTIVE

The objective of this report is to assess the capability and general characteristics of the Agilent GC-FPD/MSD with Dynatherm System (hereafter referred to as the system) to detect CW agent vapors. The intent is to provide the emergency responders concerned with CW agent detection an overview of the detection capabilities of the Agilent system.

3. SCOPE

This DP evaluation is an attempt to characterize the CW agent vapor detection capability of the Agilent GC-FPD/MSD system. Due to time and resource limitations, the agents used were limited to tabun (GA), sarin (GB), and mustard (HD). These were chosen as representative CW agents because they are believed to be the most likely threats. Test procedures follow the established DP Detector Test and Evaluation Protocol described in the Phase 1 Test Report.¹ However, due to the nature of the GC-FPD/MSD instrumentation, the DP protocol was modified to accommodate the more exploratory and time-consuming procedures required to characterize its capabilities. Given that the system is intended for use in a mobile analytical laboratory, testing of the system at temperature extremes is not deemed essential. System operation required almost weekly consultations with the manufacturer for maintenance and parameter optimization issues. The system was evaluated using the following amended test protocol:

- Evaluate the instrument at the respective allowable exposure limit (AEL), which is the 8 hr time-weighted average (TWA)² concentration level for each of the selected CW agents or find the minimum detectable level (MDL) based on optimized operational parameters.

- Evaluate the instrument using a range of CW agent concentrations, sample collection times and flow rates, and at different humidities in ambient temperatures.
- Observe the effects of potential interfering substances upon instrument performance in the laboratory and with samples collected in the field.

4. EQUIPMENT AND TEST PROCEDURES

4.1 Instrument Description.

Agilent Technologies, Incorporated (www.agilent.com), Columbia, MD, is the manufacturer of the GC-FPD/MSD tested. The system was loaned to the DP Program for inclusion in the 2001 detector evaluations. It is an instrument used for analysis and identification of unknown vapor samples at low concentrations. The system combines the sample concentrating, thermal desorption, gas chromatographic separation, selectivity of flame photometry together with the extracted ion monitoring of mass spectroscopy to identify the presence of targeted compounds (e.g., CW agents). The strength of this system is the availability of combined information and qualitative agreement between the two detection processes. A quality value (Q-value) is produced by the GC-FPD/MSD analysis. Higher Q-values represent greater certainty of the presence of the detected and identified substances.

The GC-FPD/MSD system evaluated consisted of the Agilent 6852A GC-FPD and an HP 5973 MSD, connected to a Dynatherm IACEM 980. Further information on these instruments is located at the Agilent Technologies website (<http://www.chem.agilent.com>). The 6852A GC is a 6850A GC, which has been customized for the U.S. Army Program Manager for Chemical Demilitarization and includes using two FPDs. The HP 5973 MSD is a capillary gas chromatography detector designed for use with the GC-FPD. The 6850A GC is designed to interface with an external sample introduction device (e.g., sample concentration and desorption device) to effect detection at even lower concentration levels. Vapor samples were collected using solid sorbent tubes, which were desorbed using a Dynatherm IACEM 980 thermal desorption unit (<http://www.dynatherm.com/default.asp>) connected to the GC. The Dynatherm unit thermally desorbs the sample, concentrated on the solid adsorbent tube, into the GC column for separation and analysis. The eluting substances are detected and identified using the flame photometric detector (FPD) and the HP 5973 mass selective detector (MSD).

The system is not a man portable instrument. It consists of several interconnected components and requires several compressed gas cylinders for operation. It is suited for use in a mobile analytical laboratory with a controlled environment between 15 and 35 °C. Figure 1 shows the Agilent GC-FPD/MSD with Dynatherm system as it was set up for this evaluation. The instrument was connected to a laptop computer that allowed programming of sample runs, parameter changes, and data analysis. Vapor samples were taken remotely and brought to the system for analyses. The system operates on 120 VAC and requires helium, nitrogen, hydrogen and air sources.

No Operation/Instruction Manual was provided by the manufacturer. Agilent representatives set the initial parameters for "optimum" detection capability and provided instructions to the ACT users on sample collections, Dynatherm unit operation, and operating the GC-FPD/MSD using the HP Productivity ChemStation software to analyze the samples.

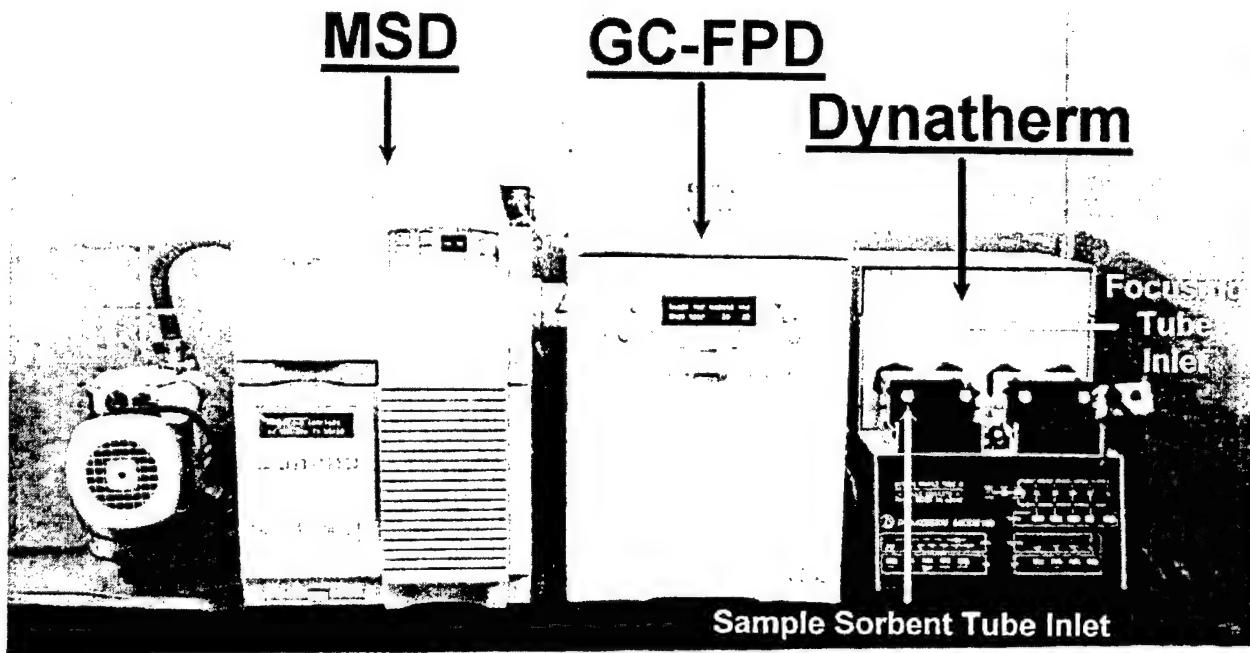


Figure 1. Agilent System: 6852A Gas Chromatograph (GC-FPD), HP Mass Selective Detector (MSD), and Dynatherm Sample Desorption Unit

The Dynatherm GC-FPD/MSD total system run time includes sample collection time, sample desorption time, the gas chromatographic elution time, plus the time required by the respective detectors (MSD and FPD) to process the elution peaks. It has the capability to permit detection of very low vapor concentrations through variation of sample collection time and rate with a minimum of 13 min required for a complete analysis cycle.

For this evaluation, the system was operated using a single FPD equipped with the phosphorus mode optical filter. There is sufficient sensitivity to detect the HD emission with the optical filter for phosphorus flame emission detection without using the more sensitive optical filter for the sulfur emission detection. This allowed both nerve (GA, GB) and blister (HD) agent

detections simultaneously. The MSD was operated in the extracted ion quantitation mode (SCAN-EIQ). This mode was used as opposed to selected ion monitoring (SIM) because, according to the manufacturer, SCAN-EIQ errs on the side of saying a compound is present even if it is not (i.e., false positive), which is the procedure dictated by the Environmental Protection Agency (EPA) for environmental analysis in the interest of public health and safety. Three to four ions from the full spectrum of each agent were chosen and used for quantification. The ions used for HD determination were at masses of 109, 111, 158, and 160. The ions used for GB were at masses 99, 125, and 81. The ions chosen for GA were at masses 70, 133, 162, and 106. When these respective qualifier ions are found and their ratios fall in line, the agent is said to be present, regardless of a spectral match.

The original GC column included with the system was 12 m long with a film thickness of 0.50 micron, and an inner diameter of 0.25 mm. This column had to be shortened to approximately 9 m to fix a break in the column after approximately 3 months of use. After another 3 months, struggling with the use of a shortened column, the column was replaced by the manufacturer with a new GC HP35 column that was 15 m long with half the film thickness (0.25 micron) and the same inner diameter of 0.25 mm. Changing the column helped resolve the separation difficulties that were experienced with the shorter column.

The Agilent GC-FPD/MSD system was designed to be a screening and confirmation tool. When an uncertainty occurs (i.e., positive identification by the FPD but not confirmed by the MSD), the system is set so that uncertainty errs on the side of caution. The system also performs an automatic library search in an attempt to identify the sample by matching it with compounds that have been entered into selected libraries. The manufacturer states that library searching and spectral matching are no substitute for operator review. The instrument can search through several libraries selected by the user. In general, the order for searching through the libraries begins with a user-generated library followed by the NIST, and then the Wiley libraries. The manufacturer recommends that a user-generated library that closely resembles the anticipated concentrations, conditions, and GC-FPD/MSD parameters be created to obtain the highest quality matches. The user is cautioned to avoid putting too much faith in the computer searched compound identification. Training and knowledge are required for positive confirmation of compound identification and good decision-making. A knowledgeable operator to manually evaluate the spectrum is necessary for increased reliability.

Depot Area Air Monitoring System (DAAMS) sorbent tubes (Tenax MX-06-2111/2035) were used for the sample collection. A sample tube is shown beside its protective glass carrying case in Figure 2. Sampling procedures are further described in Section 4.4 as the 'manual sample collection method' that is used for ACT's concentration confirmation. The Dynatherm settings used for this evaluation were selected by the Agilent representatives. Blank sorbent tube runs were repeated between samples until a clean background was observed. Several blank runs were necessary when the sample contained relatively high concentrations of either agent or contamination.

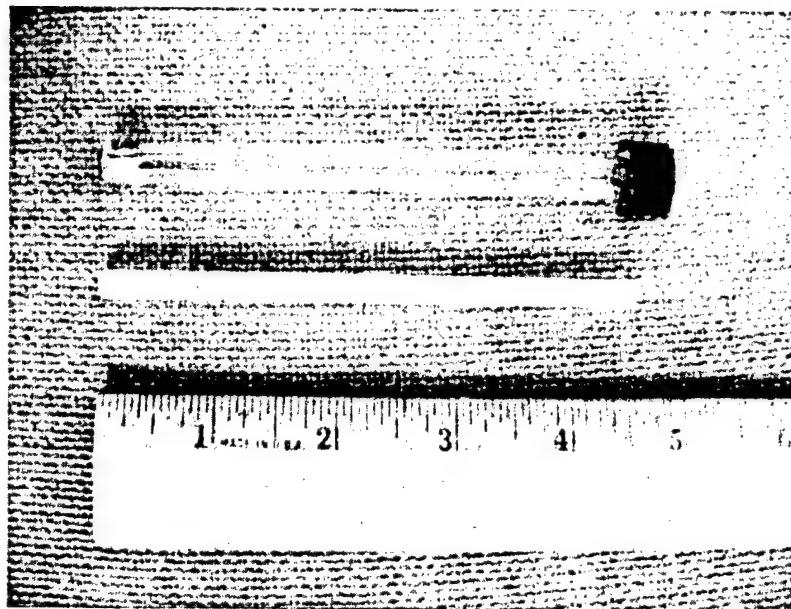


Figure 2. DAAMS Sorbent Tube and Protective Case

4.2 Calibration.

Operating procedures were followed according to the Agilent representative's instructions. Calibration of the system requires acquiring the elution peak with associated retention time for the different agents using known concentrations of liquid agent standard samples. Calibration curves for HD, GA, and GB were created within the instrument as necessary and rechecked daily for both the FPD and the MSD instruments.

Problems with the GC column that required shortening and eventual GC column change during the evaluation caused changes in retention times for all the agents. The retention times found during our evaluations included HD in the range from 5.3 to 6.45 min, GA in the range from 5.08 to 5.29 min, and GB in the range from 2.86 to 3.1 min. The similar GA and HD elution times required parameters to be re-evaluated to try to separate the peaks. Therefore, several methods were used throughout the evaluation seeking proper parameters. The evolving method with parameter changes used during the evaluation caused changes in retention times reported in this report, and new calibration curves were generated as necessary. Retention time depends on the GC column and the set parameters, and can shift slightly due to temperature fluctuations and other factors. Once the parameters and column length were fixed, retention time remained consistent between tests

4.3 Agent Vapor Challenge.

The agent challenges were conducted using the Multi-Purpose Chemical Agent Vapor Generation System³ using either Chemical Agent Standard Analytical Reference Material (CASARM) grade or the highest purity CW agents available. Agent challenge followed successful instrument calibration check. The vapor generator system permits sampling for the

instrument with humidity conditioned air without agent vapor to assure background air does not interfere before challenging it with similarly conditioned air containing the CW agent vapor. To ensure that the instrument did not exhibit undesired response peaks before agent challenges, a blank sample (no agent) was collected using the sorbent tube at the cup-like sampling port of the vapor generator and analyzed using the GC-FPD/MSD with Dynatherm system. Agent challenge begins when the solenoids of the vapor generation system are energized to switch the air streams from conditioned air only to similarly conditioned air containing the agent. Repeated samples were collected from the vapor generator at various flow rates and times to be analyzed by the system to confirm repeatability and check for any slippage (loss of sample) from the sampling tube.

The Agilent GC-FPD/MSD system was tested with the agents GA, GB, and HD at different concentration levels at ambient temperatures and medium RH in an attempt to determine the required sample volume for either AEL detection or MDL within a reasonable analysis cycle. The MDL depends on specifics, including the set parameters and sample volumes. The system was intended to provide detection and identification at either the AEL or the 8 hr TWA of the respective agents within a reasonable time.

4.4 Agent Vapor Quantification.

The generated agent vapor concentrations were analyzed independently and reported in both milligrams per cubic meter (mg/m^3) and parts-per-million (ppm) units in the data tables. The vapor concentration was quantified by using the manual sample collection methodology⁴ using the Miniature Continuous Air Monitoring System (MINICAMS[®]) manufactured by O. I. Analytical, Incorporated, Birmingham, AL. The MINICAMS[®] is equipped with an FPD and was operated in phosphorus mode for the GA and GB agents, and sulfur mode for HD.

This system normally monitors air by collection through sample lines and subsequently adsorbing the CW agent onto the solid sorbent contained in a glass tube referred to as the pre-concentrator tube (PCT). The PCT is located after the MINICAMS[®] inlet. Then the concentrated sample is periodically heat desorbed into a GC capillary column for subsequent separation, identification, and quantification. For manual sample collection, the PCT was removed from the MINICAMS[®] during the sampling cycle and connected to a measured vacuum source to draw the vapor sample from the agent generator. The PCT was then re-inserted into the MINICAMS[®] for analysis. This “manual sample collection” methodology eliminates potential loss of sample along the sampling lines and the inlet assembly when the MINICAMS[®] was used as an analytical instrument. MINICAMS[®] calibration was performed weekly and checked daily using the appropriate standards for the agent of interest. The measured mass equivalent (derived from the MINICAMS[®] chromatogram) divided by the total volume (flow rate multiplied by time) of the vapor sample drawn through the PCT produces the sample concentration that converts into milligrams/cubic meter.

4.5 Interference Tests.

The objective of the interference tests was to assess the ability of the instrument to correctly identify agent in the presence of the selected potential field interferents. Because it is

not possible to have agent vapor in the outdoor environment, it was necessary to first collect the respective substance vapor in the DAAMS sorbent tubes and then spike them with a known amount of the respective agent for evaluation. The CW agent was spiked on the sampled sorbent tubes after they were returned to the laboratory before being inserted into the Dynatherm for GC-FPD/MSD analysis.

Prior to the interference sample collection, the sample tubes were heat desorbed (blanks run through the GC-FPD/MSD with Dynatherm system using the method developed for CW agent evaluations) until the sample showed a clean background. This usually required one to three analysis cycles. The tubes were numbered and stored in sealed glass containers before and after the field test sample collection. Two sample sorbent tubes were used to sample for each substance using a sample rate of 1000 cm³/min for 5 min.

Samples of the vapors from gasoline, diesel fuel, jet propulsion fuel (JP8), kerosene, Aqueous Film Forming Foam (AFFF, used for fire fighting), household chlorine bleach, and insect repellent, 10% calcium hypochlorite solution (HTH slurry, a chlorinating decontaminant for CW agents), engine exhausts, burning fuels, and other burning materials were collected.

After return to the laboratory, the samples were spiked with a CW agent solution and analyzed using the Agilent system. When two sample tubes were available, they were crosschecked using an HD spike on one sample and a combination GA and GB spike on the second sample. Crosschecking the samples yielded information on agent identification and potential false positive results for the agent not spiked. For example, one of the two interferent samples collected was spiked with a two-component spiking solution containing the GA and GB combination to determine if the interference sample could still detect GA and GB, as well as, to determine if the sample showed a false detection of HD. The other sample that was spiked with HD would determine if the system could detect the HD in the presence of the interferent, as well as, whether the interferent caused false positive detection of either GA or GB. A three-component spiking solution containing HD, GA, and GB was used to determine if the interferent prevented the system from detecting the spiked agent if only one sample tube was available for the particular interferent.

The field tests' samples were collected outdoors at M-Field, Edgewood Area, Aberdeen Proving Ground, in July 2001. The samples were collected from open containers, truck engines, and fire-producing smoke plumes, at various distances downwind to achieve moderate concentrations (e.g., 2-15 ft for vapor fumes and 6-30 ft for smokes).

5. RESULTS AND DISCUSSION

5.1 Minimum Detectable Levels.

The determined MDL with corresponding response time for the Agilent system tested is shown in Table 1 for each agent at ambient temperatures and 50% RH. The MDL values represent analysis of samples at or below the respective AEL concentration levels for HD, GA, and GB. The MDL values are defined as the lowest CW agent concentration where repeatable responses yield results approximating the confirmed agent concentrations with, at least, an 80%

accuracy quality value (Q-value) rating for the GC-MSD analysis. The Q-value is an indication to the degree of matching between the sample elution peaks and the library mass spectra. Operator expertise is required to evaluate those output with low Q-values to assess the reliability of detection. According to the manufacturer, the library identification is contingent on the unresolved library issues. Therefore, an exact agent identification response is not considered as a requirement at present.

Total time for analysis equals the time to take a sample plus the time required for the Dynatherm and GC-FPD/MSD cycles. Therefore, the total system analysis time required 13.57 min plus the sampling time (an additional 1-10 min). Longer sampling times and higher flow rates were necessary as the concentrations decreased.

The complete cycle for the analyses shown for the MDLs in Table 1 included 10 minutes at 500 cm³/min for sampling GB, plus 3 min for sample desorption using the Dynatherm, plus 10.57 min for the GC-FPD/MSD analysis for a total time of 23.57 min for GB determination. The MDL values for GA samples were taken for 10 min at 500 cm³/min. The total time for GA determination was also 23.57 min. Attempts to collect samples at higher rates for the G agents showed possible sample slippage. The HD verification performance by the system was more successful. A 4-min sample at 1500 cm³/min was sufficient. Thus, the MDL for HD samples required 17.57 min to complete an analysis.

Calculated results derived from the system's MSD and FPD were compared with those obtained using the MINICAMS®. The calculated concentrations were consistent between instruments only at certain parameters and sample volumes. Therefore, the MDLs shown relate to the set parameters and sample volumes of the Agilent system used where the FPD and MSD correlated with the MINICAMS® determined concentrations.

The MDL concentrations are expressed in milligrams per cubic meter (mg/m³) with equivalent parts per million (ppm) values given. For comparison, the current military JSORs⁵ for CW agent sensitivity for point detection alarms, the U.S. Army's established values for immediate danger to life or health (IDLH), and the AEL are also listed in Table 1 [IDLH and AEL values are currently under review by the Centers for Disease Control (CDC)]. Army Regulation 385-61 is the source for the IDLH, AEL, and TWA values. The AR 385-61 does not establish an IDLH for HD due to concerns over carcinogenicity. The AEL values are the TWA concentration where exposure is permitted for unmasked workers in that environment for up to 8 hr.

The Agilent system was able to correctly identify HD and GB at much lower than AEL levels using various sample times and flows and an experienced operator. However, the results could not be achieved within the 900 s (15 min) JSOR constraint due to procedural requirements of system operation. The GA analysis was more difficult due to its similar elution time with HD; MDL results for GA were slightly higher than the AEL.

**Table 1. Minimum Detectable Level (MDL) and Average Response Times
at Ambient Temperatures and 50% RH for the Agilent GC-FPD/MSD System**

AGENT	Concentration in milligrams per cubic meter (mg/m ³) with parts per million (ppm) values in parenthesis, and Response Times (min)			
	Agilent System MDL	JSOR*	IDLH**	AEL***
HD	0.0005 (0.0001) in 17.57 min	2.0 (0.300) up to 2 min	N/A	0.003 (0.0005) up to 8 hr of unmasked exposure
		0.003 (0.0005) up to 15 min		
GB	0.00006 (0.00001) in 23.57 min	0.1 (0.017) up to 0.5 min	0.2 (0.03) up to 30 min of exposure	0.0001 (0.000017) up to 8 hr of unmasked exposure
		0.0001 (0.000017) up to 15 min		
GA	0.0003 (0.00004) in 23.57 min	0.1 (0.015) up to 0.5 min	0.2 (0.03) up to 30 min of exposure	0.0001 (0.000015) up to 8 hr of unmasked exposure
		0.0001 (0.000015) up to 15 min		

*Joint Service Operational Requirements for CW agent detectors (ACADA and JCAD).

** Immediate danger to life or health values from AR 385-61 to determine level of CW protection. Personnel must wear either the full ensemble with SCBA for operations or full-face piece respirators for escape.

***Airborne exposure limit values to determine masking requirements. Personnel can operate unmasked for up to 8 hr. Otherwise known as the safe TWA concentration for unmasked workers in an agent environment for 8 hr. AEL and TWA values are from the unclassified Army Regulation AR 385-61, February 1997.

5.2 Instrument Sensitivities.

The Agilent system was tested using a range of CW agent concentrations, sample volumes, times, and humidities. Tables 2, 3, and 4 show the results of these tests. The total volume of sample was varied, as was the combination of flow and time to make up the volume for sample collections (more time versus more flow). It appears there is a volume for which each sample produces a more accurate response, but a range of sample volumes can be used to yield similar results.

A higher volume of sample is needed as the concentration decreases. Higher sample volumes taken at a given concentration with a low Q-value normally produced higher Q-values (better response). Higher Q-value means more reliable identification. Ideally, Q-values of >90% are preferred and may be achieved by varying the sample volumes. However, it was observed that, although higher volume samples can yield higher Q values, the corresponding quantitative accuracy of the analysis suffers. The vapor concentration results from the system's calculated values usually showed lower than those of the actual exposure concentration.

The GC-FPD/MSD concentrations given in Tables 2, 3, and 4 are calculated from the system's analysis output. These concentrations depend on the time and flow rate in relation to the MSD response and the area response of the FPD. Except for the extremely low concentrations, the FPD and MSD instruments agreed satisfactorily with the MINICAMS® determined concentrations.

The HD relative humidity test results that were completed during this evaluation are also shown in Table 2. Samples were collected at ambient temperatures with >90% and <10% RH to assess the affect of humidity on the system's ability to detect agent. At the HD airborne exposure limit (AEL) concentrations, humidity did not appear to affect the analyses of the sample tubes. The instrument consistently demonstrated HD detection with similar results at the various humidity challenges. This was probably due to the 1 min sample drying time that was part of the Dynatherm cycle prior to the GC-FPD/MSD analysis. Due to the long analysis cycle and schedule restraints, similar RH testing using GA and GB was not completed. Given that humidity did not affect the HD detection, similar results can be expected.

5.3 Field Interference Testing.

The results of the field test interferent exposures are presented in Tables 5 and 6. Field test conditions were 26-31 °C and 53-76% RH, with gentle winds from 3-10 mph. Blank samples were taken at ambient conditions during the field test at the start of each day and several times throughout the field test evaluations to ensure no interference from outdoor conditions in the field. Two sample tubes per interference substance were collected at 1000 cm³/min for 5 min against the interferences with the exception of the doused wood fire and the burning tire. Only one sorbent tube sample was collected due to the extremely dirty smoke from these two interferences. The smokes caused the tubes to turn black.

Table 2. Agilent Responses to HD Vapor Concentrations at Various Conditions

Average Conditions		HD Challenge Concentration		Tube Sample Volume cm ³	Q-value	Calculated from Agilent Analysis Output	
Temp °C	% RH	MINICA MS® mg/m ³	ppm	Time (min) x flow cm ³ /min	%	GC-MSD Conc. mg/m ³	GC-FPD Conc. mg/m ³
26	<10	0.0012	0.0002	400	47	0.0011	*
				2000	90	0.0009	*
		0.0029	0.0004	400	73-78	0.0024	*
				2000	96-98	0.0026	*
	50-51	0.0005	0.0001	6000	97	0.0005	0.0005
		0.0012	0.0002	5000	97	0.0014	0.0010
		0.0018	0.0003	2000	98	0.0020	0.0020
		0.0020	0.0003	2000	96	0.0021	0.0023
				2000	97	0.0023	0.0021
23	>90	0.0019	0.0003	400	76-78	0.0018	*
				2000	93-99	0.0016	*

*Calculated GC results not established due to inappropriate GC calibration during these runs.

Table 3. Agilent Responses to GB Vapor Concentrations at Various Conditions

Average Conditions		GB Challenge Concentration		Tube Sample Volume cm ³	Q-value	Calculated from Agilent Analysis Output	
Temp °C	% RH	MINICA MS® mg/m ³	ppm	Time (min) x flow cm ³ /min	%	GC-MSD Conc. mg/m ³	GC-FPD Conc. mg/m ³
20-25	48-54	0.000020	0.000003	5000	26	0.00002	0.00008
		0.000035	0.000006	2000	44	0.00003	0.00003
		0.000060	0.000010	2000	89	0.00011	0.00013
				5000	80	0.00007	0.00008
		0.00008	0.000014	10000	90	0.00009	0.00008
		0.00011	0.000019	5000	87	0.00011	0.00011
		0.00014	0.000024	5000	88	0.00013	0.00015
		0.00039	0.000068	2000	98	0.00030	0.00032
		0.00058	0.00010	2000	99	0.00037	0.00037
		0.00510	0.00088	800	92	0.00515	0.00510
				2000	88	0.00501	0.00488
		0.2853	0.04980	400	97	0.2628	0.2294

Table 4. Agilent Responses to GA Vapor Concentrations at Various Conditions

Average Conditions		GA Challenge Concentration		Tube Sample Volume cm ³	Q-value	Calculated from Agilent Analysis Output	
Temp °C	% RH	MINICA MS® mg/m ³	ppm	Time (min) x flow cm ³ min	%	GC-MSD Conc. mg/m ³	GC-FPD Conc. mg/m ³
21-22	50-51	0.00005	0.000007	10000	NR	NR	0.00004
		0.00006	0.000009	5000	36	0.00002	0.00004
		0.00022	0.000033	5000	73	0.00010	0.00016
		0.00026	0.000039	2500	NR	NR	0.00025
				5000	91	0.00017	0.00019
		0.00028	0.000042	2000	NR	NR	0.00029
				5000	93	0.00016	0.00019
		0.00033	0.000049	5000	97	0.00028	0.00028
		0.0120	0.00179	2000	99	0.0140	*
		0.1700	0.02537	100	99	0.1838	0.2037
		0.1900	0.02835	2000	95	0.1635	0.1429
		0.1700	0.02537	100	99	0.1838	0.2037

NR = No response

*Calculated GC results not established due to inappropriate GC calibration.

Table 5. Interference Testing Summary (Tubes Spiked with HD only)

Type of Interference	Agent Found	Remarks
Gasoline Exhaust Idle	HD, GB	Results twice as high as expected for HD. Showed false GB positive
Gasoline Exhaust Rev	HD, GB	Results about 25% less than expected for HD. Showed false GB positive
Diesel Exhaust Idle	HD, GA, GB	Showed false GA and GB with low Q-values.
Diesel Exhaust, Rev	HD, GA, GB	HD shifted and results were higher than expected. Showed false GA and GB with low Q-values
Gasoline Vapor	HD, GB	Greater than expected HD; false GB conc.
Burning Gasoline Smoke	HD, GB	HD response doubled; False GB response
Diesel Vapor	HD, GA, GB	Slight increase in HD response; False GA indication; False GB indication but very low Q-value.
Burning Diesel Smoke	HD, GB	150% HD response; False GB indication
JP-8 Vapor	HD, GA, GB	Large false GA response with relatively high Q-value; GB false responded with very low Q-value.
Kerosene Vapor	HD, GB, GA	Relatively strong false indication of GA and GB with relatively high Q-values
Burning Kerosene Smoke	HD, GB, GA	HD conc. Depressed; Relatively strong false indication of GA and GB with relatively high Q-values
Burning Clothes	HD, GB, GA	False GA indication; Small false GB concentration with low Q-value.
AFFF Diluted	HD, GB, GA	False GA indication; Small false GB concentration with low Q-value
Bleach Vapor	HD, GB, GA	False positive indication of GB and GA with Q-Value of 33
10% HTH Vapor	HD, GB, GA	Small positive for GB; significant positive for GA with Q-Value of 33
DEET Insect Repellant	HD, GB, GA	Small positive for GB; significant positive for GA with Q-Value of 33
Burning Cardboard Smoke	HD, GB, GA	Spiked with solution including HD, GA, and GB. Smoke depressed FPD output but increased MSD output while lowering Q-values. GA Q-value was grossly affected (89 to 1).
Wood Fire Smoke	HD, GB, GA	Significant GA false positive with Q-Value of 33. GB false positive was with very low Q-value.
Doused Wood Fire	HD, GB, GA	Spiked with solution, including HD, GA, and GB. GB Q-value was grossly affected from 81 to 1; GA concentration showed significant increase with lowered Q-value.
Burning Tire Smoke	HD, GB, GA	Spiked with solution, including HD, GA, and GB. GB Q-value and FPD response were affected; GA concentration showed 3X increased with lowered Q-value.

Table 6. Interference Testing Summary (Tubes Spiked with GA and GB)

Type of Interference	Agent Found	Remarks
Gasoline Exhaust Idle	GA, GB	GA Q-value dropped from 93 to 33; No HD interference
Gasoline Exhaust, Rev	HD, GA, GB	HD false positive; GB Q-value severely affected from 80 to 1.
Diesel Exhaust Idle	HD, GA, GB	HD false positive Q-value of 1. GA concentration showed > expected concentration associated with lowered Q-value.
Diesel Exhaust, Rev	HD, GA, GB	HD false positive Q-value of 1. Both GB and GA concentration showed > expected concentration.
Gasoline Vapor	GA, GB	No HD interference; Depressed GB concentration; drastically increased the GA concentration with lowered Q-value.
Burning Gasoline Smoke	HD, GA, GB	Large false HD response; Slightly affected the determined concentrations for both GA and GB with both FPD and MS.
Diesel Vapor	HD, GA, GB	Minor false HD response; Slightly affected the determined concentrations for both GA and GB with both FPD and MS
Burning Diesel Smoke	GA, GB	Slightly affected the FPD concentrations of both GA and GB. Decreased for GB and increased for GA.
JP-8 Vapor	HD, GA, GB	FPD showed lowered GB but higher GA than expected. HD was also present. No MS results due to experimental error.
Burning JP-8 Smoke	HD, GA, GB	Lowered GB but increased GA response; HD false indication
Kerosene Vapor	HD, GB, GA	More significant increases in GA and GB for MS response than expected; HD false indication
Burning Kerosene Smoke	HD, GB, GA	More significant increases in GA for MS response than expected; False HD indication
Burning Clothes	HD, GB, GA	Significant effect in GA and GB Q-values for MS response Significant increased GA response in MS but more decreased in FPD than expected; HD false indication
FFF Diluted	HD, GB, GA	HD false indication; FPD showed 2X expected concentration for GA
Bleach Vapor	HD, GB, GA	HD false indication; Slightly inflated the GA and GB concentration.
10% HTH Vapor	HD, GB, GA	HD false indication; Slightly inflated the GA and GB concentration
DEET Insect Repellant	HD, GB, GA	HD false indication; Slightly inflated the GA and GB concentration
Burning Cardboard Smoke	HD	HD false indication; GA and GB output shifted and were not captured.
Wood Fire Smoke	HD, GB, GA	Significant effect in GA and GB Q-values for MS response Significant increased GA response in MS than expected; HD false indication
Doused Wood Fire	HD, GB, GA	Spiked with solution, including HD, GA, and GB. GB Q-value was grossly affected from 81 to 1; GA concentration showed significant increase with lowered Q-value.
Burning Tire Smoke	HD, GB, GA	Spiked with solution including HD, GA, and GB. GB Q-value and FPD response were adversely affected; GA concentration showed 3X increase with lowered Q-value.

The numbered sample tubes collected during the field test were analyzed for HD, GA, and GB. One of the two sample tubes was spiked with HD, and the other tube was spiked with a nerve agent combination (GA and GB) to assess whether the agent not spiked would be detected as a false positive and to see if the spiked agent could be identified. A combination spike of HD, GA, and GB was used when only one tube was available. The agent analysis results were one of the following: results as expected, either a higher or lower agent response than expected due to the interferent on the tube, no agent response (false negative), or a false positive for the agent that was not spiked on that tube.

As indicated in the above tables, the system's MSD, in general, was unable to provide adequate agent detection discrimination in the presence of field interferents. Analyses of the tubes after the field interferent collections, using spikes of known concentration of CW agents, showed not only false indications of CW agent but also yielded detected concentrations considerably different from the expected values. For the correctly detected peaks of the spiked agent, the MSD Q-values dropped from the high values (>80), when no interfering substance was present, to much lower Q-values (<40) and even as low as 1 with the presence of the collected field interference substance in the sample. It was extremely difficult to decide whether the detection was real or false. The FPD results were affected to a much lesser extent. However, concentrations derived from the FPD chromatographic detection were either more or less than expected without a consistent trend that could be predicted.

Further evaluations with additional potential interferent substances in the laboratory were not investigated based on the above observations and the need to return the system to the vendor.

6. CONCLUSIONS

Conclusions are based solely on the results observed during this abbreviated testing. Aspects of the detectors other than those described were not investigated.

Civilian first responders and HAZMAT personnel use immediate danger to life or health (IDLH) values to determine levels of protection for selection of personal protective equipment during consequence management of an incident. The Agilent Gas Chromatograph-Flame Photometric Detector/Mass Selective Detector (GC-FPD/MSD) with Dynatherm system was able to detect HD, GA, and GB at concentrations well below the Joint Service Operational Requirements (JSORs) and IDLH values, however, not within the time allowances. The intended use of this system is to install it in a mobile analytical laboratory. The system requires a time of 13.57 min in addition to the sample collection time for it to desorb the sample, elute through the gas chromatographic (GC) column to reach the respective detectors (MSD and FPD) to analyze the elution peaks. Relative sensitivity of the system can be achieved by varying the sample collection volume. The sampling time used is in addition to the 13.57-min run time.

The Agilent GC-FPD/MSD system was able to detect HD at 0.0005 mg/m^3 when the sample was collected for 4 min at $1500 \text{ cm}^3/\text{min}$. The Agilent system was able to detect GB at 0.00006 mg/m^3 and GA at 0.0003 mg/m^3 when the sample was collected for 10 min at

500 cm³/min. Total analysis times of up to 17.57 min for HD and 23.57 min for GB were needed for the instrument to detect allowable exposure limit (AEL)/time-weighted average (TWA) concentration levels. With a total analysis time of 23.57 min, the instrument was able to detect GA concentration slightly higher than the AEL/ TWA.

Thus, the Agilent GC-FPD/MSD system can detect at approximately TWA concentrations (0.003 mg/m³ for HD and 0.0001 mg/m³ for GA and GB) at sample times <10 min. This is well below the Joint Service Operational Requirements and IDLH concentration levels but in a timeframe that may be too long for emergency response. Results of the GC-FPD/MSD system from the field test samples that were spiked with agent after return to the laboratory showed that the analysis process is vulnerable to high probabilities of false indications. In the authors' opinions, expertise in data manipulation of the obtained chromatogram and spectra is needed to confirm whether reported results are valid. At AEL-TWA concentrations, the casual user would not be able to rely on the instrument for positive identification.

Further research with a technically knowledgeable expert is needed to search for the best parameters to use for emergency response situations. The system is very dependent on operator interpretations. It may be possible to yield more accurate agent detection and identification if the instrument included a user-generated library developed under anticipated emergency response conditions. In addition, the agent calibrations for each specific instrument (GC column and parameters may change between instruments) need to be optimized for estimated emergency incidents. Even then, the susceptibility of the instrument to become grossly contaminated would severely limit its usefulness in the field.

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